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# Influence of synthesis conditions on the properties of $Y_2O_3$–MgO nanopowders and sintered nanocomposites

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ABSTRACT

In this study, a citrate–nitrate combustion method was applied to synthesize composite $Y_2O_3$–MgO nanopowders. In order to optimize the synthesis condition to support sufficient combustion, the molar ratio of citric acid to nitrate (c/n molar ratio) used in the reaction mixtures was varied between 0.17 and 0.34. Nanopowders with an average particle size of 17 nm were achieved. The properties of these nanopowders indicated that the higher molar ratios decreased the unreacted organic components and increased the amount of carbide on the surface of the oxides, which helped to inhibit the formation of carbonate groups. The amount of carbonate groups was reduced with the increasing c/n molar ratio. $Y_2O_3$–MgO nanocomposites fabricated through hot-isostatic-pressing sintering showed a uniform distribution of $Y_2O_3$ and MgO grains, which had an average size of ~180 nm. In addition, the absorption peaks at 1410 and 1511 $cm^{-1}$ disappeared until the c/n molar ratio reached 0.28. A high average infrared transmittance of 83% in the range of 4000–1667 $cm^{-1}$ (2.5–6 μm) was obtained in the nanocomposites.


## 1. Introduction

Polycrystalline transparent ceramics have drawn considerable attention for use in infrared windows and domes because of their favorable mechanical and optical properties [1–5]. However, increased mechanical strength, improved thermal shock resistance and lower emissivity are needed to develop faster, more accurate advanced hypersonic missiles. Among the commonly available and durable mid-infrared materials, polycrystalline $Y_2O_3$ has a lower emissivity and superior high-temperature optical transmittance, but its unsatisfactory mechanical properties restrict its application in hypersonic missiles [1]. Nano-ceramics have great potential for improving the mechanical and optical properties of polycrystalline $Y_2O_3$ [6–8]. A useful method for fabricating nano-ceramics is to incorporate another phase such as MgO into the nano-ceramic. Harris [1] and Jiang [9,10] pointed out that the presence of a MgO phase inhibited the grain growth of an adjacent $Y_2O_3$ phase. This inhibited grain growth decreased the grain size and thus led to a lower critical flaw size in the ceramic material. Hence, the mechanical strength of $Y_2O_3$–MgO nanocomposites was improved to 660 MPa as predicted by Hall–Petch relation. The nanocomposites are predicted to be infrared transparent because their grain size is much smaller than the wavelength of incident light [11,12].

The fabrication of nanocomposites with fine grains, homogenous microstructures and uniform phase distribution is particularly challenging because of the need to control both the microstructural size and the elemental distribution. Several synthetic methods, such as coprecipitation, hydrothermal synthesis, flame spray pyrolysis and sol-gel combustion methods, have been developed to produce ultrafine composite nanopowders [13–18]. The sol–gel combustion method is superior to other techniques for the synthesis of $Y_2O_3$–MgO nanopowders because of its low processing temperature, precise control of the composition, and homogeneous phase distribution [19,20]. The hot-isostatic-pressing (HIP) technique, in which gas-assisted pressure is applied to pre-sintered compacts to compress them in three dimensions, has been used as a sintering technique. HIP has been found to fabricate denser ceramics with smaller grain sizes and more homogeneous microstructures than pressureless sintering or uniaxial hot-pressing (HP) sintering. [21–23].

For the sol–gel combustion method, Wang [10] chose an acetate–nitrate combustion method while Xu [24] chose a citrate–nitrate combustion method to synthesize nanopowders with particle sizes of 20 nm. Then, the authors used HIP and spark plasma sintering (SPS) techniques to fabricate $Y_2O_3$-MgO nanocomposites respectively. However, these authors failed to

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propose an effective solution for eliminating the influence of residual organic components or the formed carbonate groups in the fabricated nanocomposites, which severely damage the infrared transmittance at ~1428 $cm^{-1}$ (7 μm). Yue [25] and Marinsek [26] proved that controlling the c/n molar ratio enables making full use of the mixed reactants to obtain pure products with fewer leftover organic components. In addition, at the pre-sintering stage of HIP, residual organic components in the $Y_2O_3$–MgO nanopowders can be decomposed completely by prolonging the holding time of a low-temperature stage.

In this study, a citrate–nitrate combustion method with different c/n molar ratios was applied to synthesize $Y_2O_3$–MgO nanopowders. In order to eliminate the absorption peaks at 1410 and 1511 $cm^{-1}$ in the fabricated $Y_2O_3$–MgO nanocomposites, the effect of c/n molar ratios on the properties of nanocomposites has been analyzed. The final $Y_2O_3$–MgO nanocomposites achieved through the HIP technique exhibit excellent IR transmittance.

## 2. Experimental

$Y_2O_3$–MgO nanopowders were synthesized by a citrate–nitrate combustion method based on the redox reaction between citrate and nitrate [24]. $Y(NO_3)_3{\cdot}6H_2O$ (99.99%, Tianjin Fine Chemicals, Tianjin, China), $Mg(NO_3)_2{\cdot}6H_2O$ (99.99%, Tianjin Fine Chemicals, Tianjin, China), citric acid monohydrate (Sinopharm Chemical Reagent Co., Ltd., AR, Shanghai, China) and ethylene glycol (Sinopharm Chemical Reagent Co., Ltd., AR, Shanghai, China) were used as the starting materials. The chemicals were dissolved and mixed in deionized water based on the volume ratio of 50:50 (mole ratio of 20:80) of the oxides ($Y_2O_3$:MgO). Ethylene glycol was added to ensure the esterification reaction with citric acid for the formation of a stable polymerized network wherein metal ions were dispersed homogeneously [19]. According to concepts employed in propellant chemistry, the two idealized reactions in citrate–nitrate combustion process could be written as follows [26]:

$$6Y(NO_3)_3 + 5C_6H_8O_7 = 9N_2 + 30CO_2 + 20H_2O + 3Y_2O_3 \quad (1)$$

$$9Mg(NO_3)_2 + 5C_6H_8O_7 = 9N_2 + 30CO_2 + 20H_2O + 9MgO \quad (2)$$

The self-sustaining combustion reaction is based on the redox reaction of citric acid and nitrate. According to the chemical reactions in Eqs. (1) and (2), when the reaction is complete, the stoichiometric ratio of the citric acid and nitrate is 0.28. Thus, in order to seek a suitable proportion for the progress of the reaction, the c/n molar ratio was varied between 0.17 and 0.34, and the molar ratio of ethylene glycol/citric acid was selected to be 0.5, as shown in Table 1. The color of the synthesized nanopowders is also provided to give an intuitive view of the relationship between the c/n molar ratio and the burning efficiency. In this paper, the "ash" is the as-combusted product, and the "nanopowder" refers to the calcined product of the ash.

First, amounts of $Y(NO_3)_3{\cdot}6H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$, corresponding to a $Y_2O_3$ and MgO molar ratio of 20:80, were sequentially dissolved in distilled deionized water. Then, citric acid monohydrate and ethylene glycol were added according to the amount given in Table 1, followed by continuous stirring. After achieving a clear and colorless solution, the solution was heated at 200 °C until a porous organic foam was formed. The foam was then converted to a brown fluffy ash by a self-sustaining combustion reaction. Finally, these ashes were calcined from 200 °C to 800 °C at a heating rate of 1 °C/min and held at 800 °C for 2 h. A ball-milling process using 2 mm $ZrO_2$ balls in anhydrous alcohol was applied for 48 h to break down large agglomerates of the calcined nanopowders. After drying and sieving, the nanopowders were compressed in a stainless steel mold under a uniaxial pressure of 4 MPa. The obtained disks were further compacted using a cold isostatic pressure of 210 MPa to obtain a theoretical green density of approximately 50%. The compressed $Y_2O_3$–MgO disks were sintered first in a muffle furnace at 1400 °C for 2 h, followed by HIP (AIP, Columbus, OH) at 1350 °C for 1 h under an Ar pressure of 200 MPa. The fabricated nanocomposite disks were finally annealed at 1000 °C for 15 h in air and then polished on both sides for optical characterization.

The thermal characteristics of the organic precursor were analyzed using a combined thermogravimetric–differential thermal analysis (TG–DTA, Model 7300, EXSTAR, Japan). Powder X-ray diffraction (XRD, PANalytical X'Pert Pro, Netherlands) analysis was carried out to analyze the crystalline phases of the synthesized powders. The specific surface area of the $Y_2O_3$–MgO nanopowders was determined using a $N_2$ adsorption apparatus (Quadra–orb SI, Quantachrome Instruments, USA) based on the multipoint Brunauer–Emmett–Teller (BET) isotherm. The morphologies of the prepared samples were characterized by field emission–scanning electron microscopy (FE–SEM, ZEISS, Germany) and transmission electron microscopy (TEM, JEM-2100F, Japan). Fourier transform infrared spectroscopy (FT–IR, Nicolet 6700, Thermo Nicolet, USA) was used in the transmittance mode over a scanning range of 400–4000 $cm^{-1}$, to identify the functional groups in the powders and to measure the transmittance of the nanocomposites.

## 3. Results and discussion

Fig. 1 shows the SEM images of the ashes synthesized with c/n molar ratios of 0.17, 0.2, 0.28, and 0.34. These ashes consisted of agglomerates of different shapes and sizes. The agglomerates shown in Fig. 1a and b formed fragile hollow spheres, whereas the agglomerates shown in Fig. 1c and d formed micro-sized flakes. The hollow spheres were broken into micro-sized flakes as the c/n molar ratio increased from 0.17 to 0.34. This indicates that the higher c/n molar ratios caused the agglomerates to break apart. The role of citric acid is to form stable chelating complexes with metal ions. When the c/n molar ratio increases, more hydroxycarboxylic acid causes the cations to better distribute in the polyester medium, thus reducing the degree of particle agglomeration [27]. In addition, the increase in the c/n molar ratio will improve the propagation rate of the combustion reaction [26], and more heat will be generated. Hence, the ashes with a higher c/n molar ratio are prone to breaking under the reaction heat.

The FTIR spectra of the as-combusted products synthesized using different c/n molar ratios are shown in Fig. 2. All the samples show characteristic bands at about 3450, 1610, 1388 and 1081 $cm^{-1}$, corresponding to the O—H group, carboxyl group, carbonate group, and $NO_3$•, respectively [25,28]. The band at 850 $cm^{-1}$ also corresponds to $NO_3$•. The existence of the characteristic bands

**Table 1**
Chemical composition of the gels and color of the synthesized nanopowders.

| Sample | Citrate (mmol) | Nitrate (mmol) | Glycol (mmol) | Color of the synthesized nanopowders |
|---|---|---|---|---|
| c/n-17 | 17.0 | 100 | 8.5 | white |
| c/n-20 | 20.0 | 100 | 10.0 | grayish white |
| c/n-28 | 28.0 | 100 | 14.0 | light gray |
| c/n-34 | 34.0 | 100 | 17.0 | gray |

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